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**Due-Hansen, Johannes; Rasmussen, Søren Birk; Fehrmann, Rasmus; Christensen, Claus H.; Kustov, Arkadii**

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Danish National Research Foundation´s
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Technical University of Denmark

# Use of Biomass as a Sustainable and Green Fuel with Alkali-Resistant DeNO$_X$ Catalysts Based on Sulfated or Tungstated Zirconia

Due-Hansen J., Rasmussen S.B., Fehrmann R., Kustov A. L. and Christensen C.H.

*Center for Sustainable and Green Chemistry, Department of Chemistry, Building 206, Technical University of Denmark, DK-2800 Lyngby, Denmark*

## 1 Introduction

The use of bio-fuels as alternatives to traditional fossil fuels has attracted much attention recent years since bio-fuels belong to a family of renewable types of energy sources and do not contribute to the green-house effect. Traditional catalyst for this process suffers significant deactivation with time due to the presence of larger amounts of potassium in bio-fuels.

A possible solution of this problem is use of highly acidic supports which would interact with potassium stronger then active metal species [1, 2]. Among potential carriers, tungstated and sulfated zirconia are of high interest. Their acidic and textural properties can be modified by varying preparation conditions [3].

## 2 Catalyst Preparation

The preparation method involves two types: c*oprecipitation* of tungsten and zirconia oxides with ammonium hydroxide (AH) [4], and *precipitation* with ethyl diamine (ED) [5], illustrated in the two following schemes, respectively:

$$ZrO(NO_3)_2 \xrightarrow[2)\ NH_4OH,\ pH=9]{1)\ NH_4WO_3,\ H_2O} WO_X/Zr(OH)_4 \xrightarrow[2)\ 700°C,\ air]{1)\ 100°C,\ vac} WO_X/ZrO_2 \quad (1)$$

$$ZrO(NO_3)_2 \xrightarrow[2)\ (H_2NCH_2)_2,\ pH=9]{1)\ H_2O} Zr(OH)_4 \xrightarrow[3)\ 700°C,\ air]{1)\ 0.25N\ H_2SO_4,\ 2)\ 100°C,\ vac} SO_4/ZrO_2 \quad (2)$$

The supports are both impregnated with vandia to a concentration of 1.7-2 wt% vanadium. Poisoning with potassium is achived by incipient wetness impregation with $KNO_3$ to a K/V molar ratio at 0.2 and 0.4.

## 3 Support Characteristics

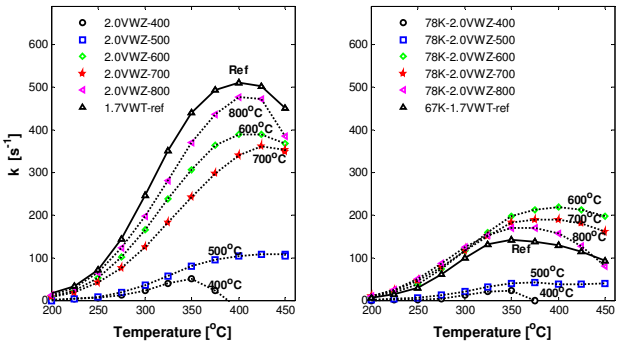
The supports were characterized through the X-ray diffraction, BET-area and ammonia-TPD. From the two latter, the concentration of acid sites can be calculated.

| Sample | Calc Temp [°C] | BET [m²/g] | Acid Conc. [µmol/m²] | Crystallinity [%] | Phase Composition$^{\beta}$ [vol%] | |
|---|---|---|---|---|---|---|
| | | | | | tet-$ZrO_2$ | mon-$ZrO_2$ |
| $WO_3/ZrO_2$-AH | 400 | 227 | 1.8 | 35.2 | a$^{\alpha}$ | a$^{\alpha}$ |
| | 500 | 167 | 2.3 | 37.1 | a$^{\alpha}$ | a$^{\alpha}$ |
| | 600 | 136 | 3.4 | 54.7 | 99.8 | 0.2 |
| | 700 | 100 | **3.8** | 64.9 | 76.8 | 23.1 |
| | 800 | 59 | 3.3 | 67.5 | 82.9 | 16.9 |
| $SO_4/ZrO_2$-AH | 700 | 85 | 3.0 | 76.1 | 51.4 | 48.6 |
| $SO_4/ZrO_2$-ED | 700 | 118 | **4.4** | 74.1 | 59.3 | 40.7 |

α Amorphous.
β Calculated with the Rietveld Refinement method. Normalized to the amount of crystalline zirconia.

**Tabel 1:** The $WO_3/ZrO_2$-AH and $SO_4/ZrO_2$-ED samples calcined at 700˚C displayed highest concentration of acid sites to which ammonia could adsorb, with 3.8 µmol/m² and 4.4 µmol/m², respectively.

## 4 NO-SCR Activity




Reference catalyst: 3.0% $V_2O_5$ +7% WO3 /$TiO_2$ (anatase).
All activities are normalized to the volume, where zirconia have a higher density than titania.

**Fig. 1:** Catalysts based on tungstated zirconia impregnated with vanadia, shows high activities in NO-SCR with ammonia, comparable with the activity of traditional catalyst (Ref). After alkali poisoning, K/V=0.2, catalysts based on tungstated zirconia calcined at 600˚C and 700˚C show the best resistance; deactivation at 350˚C is only 36% and 28%, respectively, in comparison with 68% for the reference catalyst.

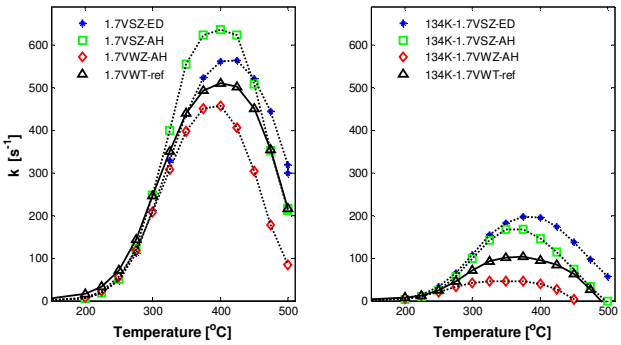



**Fig 2:** Catalysts based on sulfated supports display very high initial activities. After poisoning with potassium to K/V ratio 0.4, the reference catalyst has lost almost 80% of its initial activity at 350˚C. For the tungstated catalyst the deactivation with higher amount of potassium is also quite severe, 88%. The samples based on sulfated zirconia show best resistance towards poisoning with potassium, deactivation is 58% and 70% for the ED and AH samples, respectively.

## 5 Conclusions

Tungstated zirconia with high crystallinity shows good SCR properties and resistance towards alkali poisoning. The samples based on sulfated zirconia display very high initial SCR activities and show best resistance towards poisoning with potassium. Even though samples based on sulfated zirconia are much less affected by the poisoning with potassium, the deactivation is still quite severe indicating that potassium is eventually distributed between the acid sites of the support and active vanadia species.

## References

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